

Substitute Specification & Abstract
U.S.S.N. 10/520,106

DESCRIPTION

Activation Energy Ray Sensitive Resin Composition,
Activation Energy Ray Sensitive Resin Film and
Method for Forming Pattern Using the Film

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CROSS-REFERENCE TO RELATED APPLICATIONS

[0001] This application is a National Phase Application
(35 USC 371) of PCT/JP2003/008539 and claims priority of
10 Japanese Application No. 2002-196577 filed April 7, 2002.

Technical Field:

[0002] This invention relates to an activation energy
ray-sensitive resin composition containing an acid former
15 which generates an acid by the action of activation
radiation and which is dispersed in an aqueous solution
of a water-soluble resin, in the presence or absence of a
sensitizer, to which an acid-reactive insolubilizing
agent is added. The invention further relates to an
20 activation energy ray-sensitive resin film obtainable
from the above composition, and to a method for forming a
pattern using the film.

Background Art:

[0003] An activation energy ray-sensitive resin or
resin composition is utilized for covering a surface of
an image forming substrate. This resin undergoes a change
in chemical structure created by the action of activation
energy rays such as light, infrared rays, far-infrared
25 rays, electron beams or X-rays. Among these energy forms,
light is widely used. For this reason, the following
description occasionally specifically refers to light as
the activation energy. However, the activation energy
utilized with the composition and films according to the
30 present invention is not limited to light.
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[0004] Resins which are sensitive to light and compositions containing same are utilized in many fields and in large quantities as pattern forming materials having high resolution in photolithography, etc. (see 5 "Photopolymer Technology", edited by YAMAOKA, Tsuguo and MATSUNAGA, Gentaro, Nikkan Kogyo Shimbun Ltd. (1988))

Polymer-type photosensitive materials, have not only good resolution but also provide a wide range for setting of a photosensitive region for use with a selected wavelength 10 of light. Further, they have an important utility as resin layers which can be patterned by irradiation with light and can thereby serve as a resist material in the chemical, physical or mechanical etching of a substrate. Further, they are actually used as a platemaking material 15 for letterpress printing, intaglio printing, lithography or stencil printing. By virtue of these characteristics, they are utilized as photolithographic materials encompassing a wide range from submicrons to centimeters.

[0005] In the case of a polymer-type photosensitive 20 resin, patterns are formed through a development treatment which utilizes a change in a physical property, such as solubility, caused as a result of a change in chemical structure in the exposed or unexposed region. When the resin is used as a surface covering, a change in 25 chemical structure caused by light exposure induces a significant change in a physical property to provide for protection of a substrate. Such a change in chemical structure of the resin is not attributed to the photochemical reaction alone; rather, the change is based 30 on the combined effect of a number of chemical reactions, inclusive of various secondary reactions induced by the photochemical reaction. Thus, for example, it is possible to arbitrarily select the solubility of a resin layer in a solvent before and after light exposure. Namely, when 35 the solubility of the exposed region decreases, the resin

serves as a negative-type photosensitive resin in solvent developing. When the solubility of the exposed area is increased, then the resin serves as a positive-type photosensitive resin.

5 [0006] When patterning is effected by development with a solvent, it is indispensable to use water as a solvent which is cheapest and safest, since it is directly related to environmental problems including work environment and waste treatment. When water which is
10 neutral and which has high polarity is used as a solvent, it is required that the material to be dissolved therein should also have a high degree of polarity. Therefore, examples of photosensitive resin capable of being developed with neutral water are restricted as will be
15 described hereinafter.

[0007] From the foregoing viewpoint, the production of photosensitive films which can be developed using neutral water by itself as a solvent and the provision of a photosensitive resin or a photosensitive resin
20 composition capable of being developed with neutral water alone have long been sought. However, there are available only a limited number of photosensitive resins capable of being developed with neutral water as will be described hereinafter. Whilst a photosensitive resin which
25 comprises a water-soluble polymer, such as gelatin, casein or poly(vinyl alcohol), and a dichromate added thereto, has been used in practice in the past, its utilization has been restricted or excluded, since it contains heavy metal ions and since it has poor storage stability. Similarly, a photosensitive resin using a water-soluble diazo resin as a photo-crosslinking agent and containing a water-soluble polymer as mentioned above has been widely utilized. However, the range of utilization of the resin is limited because the
30 photosensitivity is lower than that of a dichromate-type
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photosensitive resin, because the resin is ill-suited for a thick photosensitive layer due to coloring of the exposed area and resulting reduction in light transmittance and because the problem of long-term storage stability remains unsolved. Further, there has been proposed a composition in the form of an emulsion of an ethylenically unsaturated compound and a photopolymerizable initiator in poly(vinyl alcohol), and a photo-crosslinking agent blended into the emulsion (Japanese Unexamined Patent Publications No. S49-121852, No. S50-108003, No. S59-107343, etc.). Such a composition, however, is unsatisfactory with respect to the water resistance, since no crosslinkages are formed in the poly(vinyl alcohol) itself.

[0008] Materials containing poly(vinyl alcohol) to which hydrophilic residues, e.g., styrylpyridinium, are bonded have been proposed as water-soluble photosensitive polymers that solve the foregoing problems (Japanese Unexamined Patent Publications No. S55-23163, No. S55-62905, No. 58-25303, etc.). These materials have merit in that the sensitivity thereof is higher than that of the above-described water-developing-type photosensitive resins and in that the storage stability is excellent and, therefore, have use as pattern forming materials, representative of which is a screen platemaking material. However, since the water-insolubilization of the photosensitive polymer is attained only by a photodimerization reaction, there is no great change in physical properties, e.g., hydrophilicity, although the change in solubility in neutral water before and after the light exposure is significant. As a consequence, when the polymer is used as a printing platemaking material, it has poor resistance to an aqueous ink. Therefore, improvement of the physical property of the polymer is sought by using various additives. For example,

compositions blended with an aqueous emulsion are proposed in Japanese Unexamined Patent Publications No. S55-62446, No. S60-10245, No. S61-17141, No. 56-122784, No. S60-10245, etc. However, problems in various physical properties such as water resistance and mechanical strength still remain unsolved.

[0009] Thus, resist materials have been widely adopted, wherein an acidic group such as a carboxyl group or a phenolic hydroxyl group is produced by the catalytic action of an acid generated as a result of a photochemical reaction, the acidic group being utilized for solubilization of the resist in an aqueous alkali solution. With this method, a positive-type or negative-type pattern can be formed by development with an aqueous alkali solution (see C. P. Wong, Polymers for Electronic and Photonic Applications, Academic Press, p.67 (1993)). Because these constituents are insoluble or sparingly soluble in water, the composition is prepared as an organic solvent solution. As a consequence, there arises a problem in that the organic solvent evaporates and disperses during the coating operation for forming a film. In a photolithographic process with production on an extremely large scale, it is necessary to neutralize the developing liquid before discarding. Additionally, depending upon the intended use, there arises the problem that the physical properties of the pattern resist layer will deteriorate due to the presence of acidic groups having a high polarity formed in the exposed area. On the other hand, a method has also been proposed in which alkaline residues, representative of which is an amino group, are formed by photochemical reaction and in which development is carried out using acidic water. Since, however, a film coating step using an organic solvent must be included in this method, addition of a neutralizing treatment becomes unavoidably necessary in

the alkali development.

[0010] Thus, in photosensitive compositions containing an acid generating agent, it is general practice to dissolve the acid generating agent in * a solvent or other liquid component. As a consequence, when the solvent for the photosensitive composition and the solvent for development are limited to water, it is necessary that the acid generating agent or a photosensitizer therefor should be soluble in water.

10 Japanese Unexamined Patent Publication No. H09-319080 proposes a water-developable photosensitive composition containing poly(vinyl alcohol), a crosslinking agent and a water-soluble acid generating agent. The composition has a problem because the type of the water-soluble acid generating agent is restricted and because the acid generated is a carboxylic acid which is low in acidity.

15 On the other hand, Japanese Unexamined Patent Publication No. H10-62990 proposes a photosensitive composition for screen printing which is developable with water and which

20 is prepared by emulsifying a liquid epoxy resin in an aqueous solution of poly(vinyl alcohol) containing a cationic photoinitiator to form an oil-in-water type emulsion. In actual practice, however, a diazo resin or dichromate is added as a water-soluble photo-crosslinking

25 agent or the composition uses poly(vinyl alcohol) into which a photo-crosslinkable stilbazolium group has been introduced. The reason is that, because the liquid epoxy resin containing the cationic photoinitiator is emulsified in the aqueous solution of poly(vinyl alcohol),

30 the reaction of the acid generated by irradiation of a resin film made of the composition with the hydroxyl groups of the poly(vinyl alcohol) which is in a discontinuous phase from the epoxy resin does not easily occur, though the acid generated can induce the cationic

35 polymerization of the epoxy resin. Thus, the proposed

composition has a problem that crosslinking does not sufficiently proceed in the absence of the photo-crosslinking agent.

[0011] Thus an object of the present invention is to
5 provide an activation energy ray-sensitive resin composition which is capable of being developed with neutral water, an activation energy ray-sensitive resin film obtainable from the composition, and a pattern forming method using the film.

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SUMMARY OF THE INVENTION

[0012] In accordance with the present invention, there are provided an activation radiation-sensitive resin composition which is capable of being developed with
15 neutral water, an activation radiation-sensitive resin film which is capable of being developed with neutral water, and a pattern forming method as follows.

[0013] (1) The activation energy ray-sensitive (hereinafter "radiation-sensitive") resin composition of
20 the invention comprises:

a dispersion comprising an aqueous solution of a water-soluble resin, an acid former which generates an acid when activated by radiation and which is insoluble or sparingly soluble in water, and a sensitizer for
25 sensitizing the acid forming reaction, said acid former and sensitizer being dispersed in said aqueous solution in the form of fine powder, and

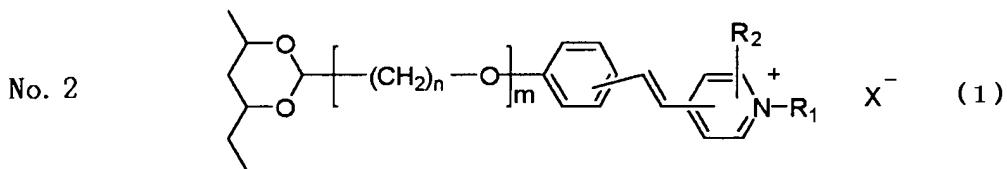
an acid-reactive insolubilizing agent dissolved or dispersed in said dispersion and insolubilizing said
30 water-soluble resin by the action of said acid.

[0014] The radiation-sensitive resin may be a compound having at least one radical polymerizable unsaturated bond.

[0015] The acid-reactive insolubilizing agent may be an
35 N-methyolated or N-alkoxymethylated nitrogen-containing

compound, a hydroxymethylated phenol derivative or a resol resin. Alternatively, the acid-reactive insolubilizing agent may be a compound having at least one epoxy group, oxetane group, vinyloxy group, 5 isopropenyloxy group or orthoester group, formyl group or acetal group.

[0016] Any of the radiation sensitive resin compositions described above may be in the form of an aqueous resin emulsion. Optionally, the radiation-sensitive resin composition further comprises a water-soluble, photo-insolubilizable resin which may be a photo-crosslinkable poly(vinyl alcohol) into which a styrylpuridinium group represented by the following general formula (1) has been introduced:



wherein R₁ represents a hydrogen atom, an alkyl group or an aralkyl group, R₂ represents a hydrogen atom or a lower alkyl group, X⁻ represents a halogen ion, a phosphate ion, a p-toluenesulfonate ion or a mixture of these anions, m is a number of 0 or 1 and n is an integer of 1 to 6. In 15 one preferred embodiment the water-soluble, photo-insolubilizable resin comprises poly(vinyl alcohol), casein or gelatin, and a water-soluble diazo resin or a dichromate.

[0017] Any of the above-described radiation-sensitive resin compositions may be formed into a film. Such a film may be used for a screen printing process and in pattern forming methods wherein the radiation sensitive resin film is irradiated with activation radiation and then 20 developed with water, optionally after having been heat-treated for facilitating the acid-catalyzed

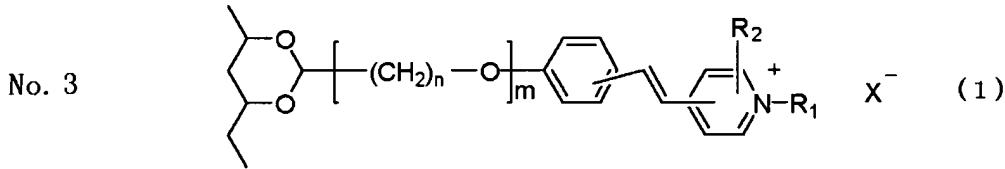
insolubilization reaction.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

[0018] The water-soluble resin serving as a dispersing agent for finely dispersing the acid former and/or sensitizer in the present invention, may be any naturally occurring polymer, semi-synthetic polymer or synthetic polymer (refer to "Development Techniques of Water-Soluble Polymers", CMC (1999)). Suitable naturally occurring polymers include chitin, chitosan, casein, collagen, albumen, starch, carrageenan, xanthan gum, dextran, pullulan, etc. Suitable semi-synthetic polymers include dialdehyde starch, partial hydrolysate of starch, hydroxyethyl starch, cyclodextrin, dextrin, carboxymethyl cellulose, methyl cellulose, hydroxyethyl cellulose, hydroxypropyl cellulose, etc. Suitable synthetic polymers include poly(vinyl alcohol), partially saponified poly(vinyl alcohol), poly(vinyl alcohol) acetalized such that the water solubility is not lost, poly(vinylpyrrolidone) and copolymers thereof, polyacrylamide and copolymers thereof, N-isopropylacrylamide and copolymers thereof, acrylamide and copolymers thereof, N,N-dimethylacrylamide and copolymers thereof, poly(N-acetylvinylamine), polyethylene glycol, etc.

[0019] Polymers having basic residues may also be used for the purpose of the present invention, since reduction of the acidity generated by the acid former can be prevented by adjusting the pH of the aqueous solution to about 7. However, it is preferred that the water-soluble polymer chains be free of amino groups which are basic residues or that the amount of amino groups be as small as possible. It is also preferred that the water-soluble polymers contain functional groups capable of reacting with the acid-reactive insolubilizing agent, such as

- hydroxyl groups. In this regard, starch, dialdehyde starch, methyl cellulose, hydroxyethyl cellulose, hydroxypropyl cellulose, poly(vinyl alcohol), polyacrylamide, hydroxyethyl acrylate copolymers, 5 hydroxyethyl methacrylate copolymers, water-soluble N-methyloated nylon, etc. are suitably used. Since these water-soluble polymers also function as a dispersant for the solid photo-acid former, cationic residues may be introduced thereinto.
- 10 [0020] These water-soluble resins may be added as a binder resin to a fine dispersion of the acid former and/or sensitizer. Further, these water-soluble binder resins may be used together with a diazo resin or a dichromate as a photo-crosslinking agent. Furthermore, a 15 photo-crosslinkable poly(vinyl alcohol), disclosed in Japanese Unexamined Patent Publications No. S55-23163, No. 55-62905, etc. and containing a styrylpyridinium group represented by the general formula (1) shown below, may be suitably used as the binder resin:



20 In the above formula, R_1 represents a hydrogen atom, an alkyl group or an aralkyl group, R_2 represents a hydrogen atom or a lower alkyl group, X^- represents a halogen ion, a phosphate ion, a p-toluenesulfonate ion or a mixture of these anions, m is 0 or 1 and n is an integer of 1 to 6. 25 The alkyl group R_1 has 1 to 6 carbon atoms, preferably 2 to 4 carbon atoms. The aralkyl group R_1 has 7 to 13 carbon atoms, preferably 7 to 10 carbon atoms. The aralkyl group may be derived from various aromatic 30 compounds (benzene compounds, naphthalene compounds, anthracene compounds, etc.) having alkyl groups. The

lower alkyl group R₂ has 1 to 4 carbon atoms, preferably 1 to 2 carbon atoms.

[0021] The acid former which generates an acid by the action of activation radiation according to the present invention, may be a compound utilized in chemical amplification-type photoresists or in cationic photopolymerization (refer to "Organic Materials for Imaging", edited by Organic Electronics Material Study Group, Bunshin Shuppan (1993)). Suitable acid formers for use in the present invention include cationic onium compounds, halogen-containing compounds which generate a hydrogen halide, and sulfonated compounds which generate sulfonic acid. These compounds are insoluble or sparingly soluble in water. Examples of such suitable compounds are given below.

[0022] Suitable ionic acid formers include salts of onium cations, such as diazonium, ammonium, iodonium, sulfonium, phosphonium or ferrocenium, with Cl⁻, Br⁻, I⁻, ZnCl₃⁻, HSO₃⁻, BF₄⁻, PF₆⁻, AsF₆⁻, SbF₆⁻, CH₃SO₃⁻, CF₃SO₃⁻, perfluorobutanesulfonate, perfluorooctanesulfonate, camphorsulfonate, benzenesulfonate, p-toluenesulfonate, 9,10-dimethoxyanthracene-2-sulfonate, cyclohexylamino sulfonate, (C₆F₅)₄B⁻, (C₄H₉)₄B⁻, etc.

[0023] Specific examples of the cationic onium compounds include phenyldiazonium, p-methoxy diazonium, α -naphthyldiazonium, biphenyldiazonium, diphenylamine-4-diazonium, 3-methoxydiphenylamine-4-diazonium, 2,5-diethoxy-4-methoxybenzoylamidophenyldiazonium, 2,5-diproxy-4-(4-tolyl)thiophenyldiazonium, 4-methoxydiphenylamine-4-diazonium, condensate of 4-diazodiphenylamine and formaldehyde, 1-methoxyquinolinium, 1-ethoxyisoquinolinium, 1-phenacylpyridinium, 1-benzyl-4-benzoylpyridinium, 1-benzylquinolinium, N-substituted benzothiazolium (refer to Japanese Unexamined Patent Publication No. H05-140143), etc. Further examples

include benzyltriphenyl sulfonium, p-methoxyphenyldiphenyl sulfonium, bis(p-methoxyphenyl)phenyl sulfonium, tris(p-methoxyphenyl) sulfonium, p-phenylthiophenyldiphenyl sulfonium, benzyltetramethylene sulfonium,
5 phenacyltetramethylene sulfonium, phenacyldimethyl sulfonium, p-methoxyphenydiethyl sulfonium, naphthyldialkyl sulfonium (refer to Japanese Unexamined Patent Publications No. H09-118663 and No. H05-140209), (2-naphthylcarbonylmethyl)-tetramethylene sulfonium, (p-
10 hydroxyphenyl)dimethyl sulfonium, (4-hydroxynaphthyl)dimethyl sulfonium, (4,7-dihydroxynaphthyl)-1-dimethyl sulfonium, (4,8-dihydroxynaphthyl)-1-dimethyl sulfonium, diphenyl iodonium, phenyl(4-methoxyphenyl) iodonium, phenyl{4-(tert-butyl)phenyl}iodonium, 4-bis{4-(tert-butyl)phenyl}iodonium, bis(4-dodecylphenyl) iodonium, (4-methoxyphenyl)-4-octyloxyphenyl) iodonium,
15 phenacyltriphenyl phosphonium, cyanomethyltriphenyl phosphonium, etc.

20 [0024] Examples of suitable acid formers generating a halogenated hydroacid include 1-methyl-3,5-bis(trichloromethyl)-s-triazine, 1-phenyl-3, 5-bis(trichloromethyl)-s-triazine, 1-(4-chlorophenyl)-3, 5-bis(trichloromethyl)-s-triazine, 1-(4-methoxyphenyl)-3, 5-bis(trichloromethyl)-s-triazine, 1-(4-butoxyphenyl)-3, 5-bis(trichloromethyl)-s-triazine, 1-(3, 4-methylenedioxyphenyl)-3, 5-bis(trichloromethyl)-s-triazine, 1-(3,4-dimethoxyphenyl)-3, 5-bis(trichloromethyl)-s-triazine, 1-(4-methoxynaphthyl-1)-3, 5-bis(trichloromethyl)-s-triazine, 1-{2-(4-methoxyphenyl)ethenyl}-3, 5-bis(trichloromethyl)-s-triazine, 1-{2-(2-methoxyphenyl)ethenyl}-3, 5-bis(trichloromethyl)-s-triazine, 1-{2-(3, 4-dimethoxyphenyl)ethenyl}-3, 5-bis(trichloromethyl)-s-triazine, 1-{2-(3-chloro-4-methoxyphenyl)ethenyl}-3, 5-bis(trichloromethyl)-s-triazine,

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1-(biphenyl-1)-3,5-bis(trichloromethyl)-s-triazine, 1-(4-hydroxybiphenyl-1)-3,5-bis(trichloromethyl)-s-triazine, 1-(4-methoxybiphenyl-1)-3,5-bis(trichloromethyl)-s-triazine, 1-(4-methylbiphenyl-1)-3,5-bis(trichloromethyl)-s-triazine, 1,3,5-tris(trichloromethyl)-s-triazine, 1,3-dichloro-4-trichloromethylbenzene, 1,1,1-trichloro-{2,2-84-chlorophenyl}ethane, phenyltribromomethyl sulfone, 1-keto-4-methyl-4-trichloromethyl-2,5-dichlorohexadiene, 2-tribromoquinoline and 1-keto-2,3-benzo-4,4,5,6-tetrachlorohexadiene.

[0025] Suitable acid formers which generate sulfonic acids include 2-nitrobenzyl-p-toluene sulfonate, 2,6-dinitrobenzyl-p-toluene sulfonate, 1-(p-toluenesulfonyloxyimino)-1-phenylethane nitrile, 1-(p-toluenesulfonyloxyimino)-1-phenylethanenitrile, benzoin-p-toluenesulfonate, 2-p-toluenesulfonyloxy-2-benzoylpropane, p-nitrobenzyl-9,10-dimethoxyanthracene-2-sulfonate, N-trifluoromethanesulfonyloxydiphenylmaleimide, N-p-toluenesulfonyloxysuccinimide, N-camphorsulfonyloxysuccinimide, N-trifluoromethanesulfonyloxysuccinimide, N-perfluorobutanesulfonyloxysuccinimide, N-p-toluenesulfonyloxyphthalimide, N-camphorsulfonyloxyphthalimide, N-trifluoromethanesulfonyloxyphthalimide, N-perfluorobutanesulfonyloxyphthalimide, N-p-toluenesulfonyloxy-1,8-naphthalenecarboxyimide, N-camphorsulfonyloxy-1,8-naphthalenecarboxyimide, N-trifluoromethanesulfonyloxy-1,8-naphthalenecarboxyimide, N-perfluorobutanesulfonyloxy-1,8-naphthalenecarboxyimide, 1,2,3-tris(p-toluenesulfonyloxy)benzene, bis(phenylsulfone), bis(phenylsulfonyl)methane, etc.

[0026] The above-described acid formers which are insoluble or sparingly soluble in water are finely

dispersed in the aqueous solution of the water-soluble resin. Therefore, the acid generated by activation radiation can easily diffuse into the water-soluble resin. As a consequence, the acid-catalyzed reaction of the 5 acid-reactive insolubilizing agent and the water-soluble resin is facilitated so that the insolubilization of the resin can efficiently proceed.

[0027] In the present invention, while the acid formers mentioned above can generate, by themselves, the 10 corresponding acid by the action of activation radiation, the acid can be also generated when they are irradiated, in the presence of a spectrum sensitizer, with light which can be absorbed by the sensitizer. The spectrum sensitizer used for the purpose of the present invention 15 is desirably insoluble or sparingly soluble in water. Thus, the desired objects may be achieved when the acid former is dispersed together with the sensitizer in the form of fine powder. It was unexpected that the sensitized acid forming reaction efficiently gave 20 insolubilization even when not only the acid former but also the sensitizer is in the form of dispersed solids.

[0028] The sensitizer used in the present invention is preferably an electron donating compound in view of the fact that the above-exemplified acid formers function as 25 electron donors, as described in Japanese Unexamined Patent Publications No. S54-151024, No. S58-40302, No. S60-76740, No. S60-78443, No. S60-88005, No. S60-112802, No. S61-97650, No. S61-180359, No. S62-161820 and No. S63-243102. Such sensitizers suitable for the present 30 invention include, but are not limited to, aromatic polycyclic compounds, porphyrin compounds, phthalocyanine compounds, polymethine dye compounds, merocyanine compounds, coumarin compounds, thiopyrylium compounds, pyrylium compounds, p-dialkylaminostyryl compounds, 35 thioxanthene compounds, etc. Most of these compounds are

disclosed in "Dye Handbook" (Kodansha) edited by Ookawara, Hirashima, Matsuoka and Kitao; "Handbook of Coloring Material Engineering" (Asakura Publishing (1989)), edited by the Japan Society of Coloring Material; and "Dye Catalogue" of Hayashibara Biochemical Laboratories Photosensitive Dye Lab.

5 [0029] Suitable aromatic polycyclic compounds include those which have a basic skeleton of a hydrocarbon such as naphthalene, phenanthrene, pyrene, anthracene, tetracene, chrysene, pentacene, picene, coronene, hexacene or ovalene. Also, aromatic five-membered ring heteropolycyclic compounds containing an oxygen atom, a nitrogen atom or a sulfur atom, such as benzofuran, dibenzofuran, indole, carbazole, benzothiophene and dibenzothiophene, may be used. Usable aromatic six-membered ring heteropolycyclic compounds have a basic skeleton of, for example, α -benzopyrone, β -benzopyrone, α -thiabenzopyrone, β -thiabenzopyrone, flavone, xanthone, thioxanthone, phenoxazine or phenothiazine. These basic skeletons may have at least one electron donating group such as an alkyl group, a hydroxyl group, an alkoxy group or an alkylthio group. Examples of the sensitizers in the form of substituted aromatic polycyclic compounds include 1-methoxynaphthalene, 1,4-dimethylnaphthalene, 1,8-dimethylnaphthalene, 9,10-dimethylphenanthrene, 9-methylantracene, 9,10-dimethylantracene, 9,10-diphenylanthracene, 9,10-bis(phenylethynyl)anthracene, 1,8-dimethyl-9,10-bis(phenylethynyl)anthracene, 9,10-dimethoxyanthracene, 9,10-diethoxyanthracene, 9,10-dipropoxyanthracene, 9,10-dibutoxyanthracene, and 1-methylpyrene. Suitable substituted polycyclic heterocyclic compounds include N-methylcarbazole, N-ethylcarbazole, thioxanthone, isopropylthioxanthone, etc.

10 [0030] The porphyrin compound may be a compound having a basic skeleton of, for example, tetraphenylporphine,

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octaethylporphine, mesoporphyrin, protoporphyrin, hematoporphyrin, chlorin, tetrabenzoporphine, phenyl-substituted tetrabenzoporphine, a magnesium complex thereof, or a zinc complex thereof. Also, suitable is 5 chlorophyll.

[0031] The phthalocyanine compound may be a naphthocyanine compound and may have at least one substituent, such as an alkyl group, an alkoxy group, an alkylthio group, an aryl group or a halogen group, 10 introduced into its basic skeleton. Further, as a central metal, magnesium, zinc, cadmium or aluminum is particularly preferred.

[0032] As the polymethine dye compound, a cyanine-series or merocyanine-series compound having a 15 heterocyclic structure containing a nitrogen atom, an oxygen atom, a sulfur atom, etc., bound to polymethine can be used. Such compounds are disclosed, for example, in "Dye Handbook" edited by Makoto OOKAWARA, Teijiro KITAO, Tsuneaki HIRAOKA and Ken MATSUOKA, (Kodansha Scientific (1986)), pages 382-417. Specific examples of 20 the dye compounds include cyanine-compounds comprising a quinoline ring, indiocyanine compounds comprising an indole ring, thiocyanine compounds comprising a benzothiazole ring, and polymethine compounds comprising 25 an iminocyclohexadiene ring. Additionally, benzoxazole compounds, pyrylium compounds, thiapyrylium compounds, squarylium compounds, and croconium compounds may be used.

[0033] The coumarin compound may be chosen from among the monocoumarin compounds described in "Dye Handbook" 30 edited by Makoto OOKAWARA, Teijiro KITAO, Tsuneaki HIRAOKA and Ken MATSUOKA, (Kodansha Scientific (1986)), pages 432-438 and, additionally, 3-(2-benzothiazolyl)-7-(diethylamino)coumarin, 3-(2-benzothiazolyl)-7-(dibutylamino)coumarin, 3-(2-benzothiazolyl)-7-(dioctylamino)coumarin, 3-(2-benzo imidazolyl)-7-

- (diethylamino)coumarin, 10-(2-benzothiazolyl)-2,3,6,7-tetrahydro-1,1,7,7-tetramethyl-1H,5H,11H-[1]benzopyrano[6,7,8-ij]quinolyzin-11-on, 3,3-carbonylbis(7-diethylaminocoumarin), 3,3-carbonylbis(7-dibutylaminocoumarin), etc.
- 5 [0034] Suitable p-dialkylaminostyryl compounds include 4-diethylaminobenzylideneacetophenone, 4-diethylaminobenzylidene(p-methoxy)acetophenone, 4-diethylaminobenzylidenemalondinitrile,
- 10 4-dimethylaminobenzylideneacetoacetic ethyl ester, 4-dimethylaminobenzylidenemalonic acid diethyl ester, 4-dimethylaminobenzylidene- α -cyanoacetophenone, 2,6-bis(4-dimethylaminobenzylidene)cyclohexanone, 4-dimethylaminocinnamylideneacetophenone,
- 15 4-dimethylaminocinnamylidenemalondinitrile, 4-dimethylaminocinnamylidenecyanoacetic acid ethyl ester, 4-dimethylaminocinnamylidenemalonic acid diethyl ester, 4-dimethylaminocinnamylidene- α -cyanoacetophenone, 4-dimethylaminocinnamylidenebis(4-
- 20 dimethylaminobenzylidene)cyclohexanone, etc.
- [0035] The absorption wavelengths of these sensitizers encompass a wide range from ultraviolet to infrared. Thus, they can be used singly or as a mixture of two or more thereof so that light of a wide range of wavelengths can be efficiently absorbed for the generation of the acid. The term "acid-reactive insolubilizing agent" as used herein is intended to refer to a compound which causes dehydrative condensation reactions, addition reactions, cationic polymerization reactions, etc. by the catalytic action of the acid generated by the activation radiation, so that the water-soluble resin contained in the composition is insolubilized through crosslinking, polymerization, etc. In particular, it is preferred that the insolubilizing agent be acid-catalytically bonded to the main chain or side chain cites of the water-soluble

resin. The insolubilizing agent may be soluble, insoluble or sparingly soluble in water. An insolubilizing agent which is insoluble or sparingly soluble in water may be used in the form of a dispersion. The insolubilizing agents mentioned below may be used alone or as a mixture of two or more thereof.

[0036] Insolubilizing agents which undergo dehydrative condensation with alcoholic hydroxyl groups of poly(vinyl alcohol), cellulose derivatives, polysaccharides such as starch, N-methylolated nylon, etc. as the water-soluble resin, include N-hydroxymethylacrylamide, N-hydroxymethylated urea, N-hydroxymethylated malonamide, N-hydroxymethylated phthalamide, hexahydroxymethylated melamine, p-hydroxymethylphenol, o-hydroxymethylphenol, 2,6-bis(hydroxymethyl)-p-cresol, resol resin, etc. Derivatives of these compounds in which the hydroxymethyl group is replaced by an alkoxyethyl group having 1-6 carbon atoms may also be used.

[0037] Suitable insolubilizing agents which undergo an addition reaction with alcoholic hydroxyl groups of poly(vinyl alcohol), cellulose derivatives, polysaccharides such as starch, and derivatives thereof as the water-soluble resin, include compounds having at least one epoxy group or oxetane group. Such a compound also causes cationic polymerization and is particularly preferred. Suitable insolubilizing agents having two or more glycidyl-type epoxy groups, include EX-611, EX-612, EX-614, and EX-614B EX-614, EX-622, EX-512, EX-521, EX-411, EX-421, EX-313, EX-314, EX-321, EX-201, EX-211, EX-212, EX-252, EX-810, EX-811, EX-850, EX-851, EX-821, EX-830, EX-832, EX-841, EX-861, EX-911, EX-941, EX-920, EX-721, EX-221, EM-150, EM-101 and EM-103, which are DENAKOL-series products described in a catalog of Nagase Chemtex Co., Ltd.; YD-115, YD-115G, YD-115CA, YD-118T and YD-127, which are described in a catalog of Toto Kasei

Co., Ltd.; and 40E, 100E, 200E, 400E, 70P, 200P, 400P, 1500NP, 1600, 80MF, 100MF, 4000, 3002 and 1500, which are EPOLITE-series products described in a catalog of Kyoeisha Chemical Co., Ltd. Suitable alicyclic epoxy 5 compounds include CELOXIDE 2021, CELOXIDE 2080, CELOXIDE 3000, EPOLEAD GT300, EPOLEAD GT400, EPOLEAD D-100ET, EPOLEAD D-100OT, EPOLEAD D-100DT, EPOLEAD D-100ST, EPOLEAD D-200HD, EPOLEAD D-200E, EPOLEAD D-204P, EPOLEAD D-210P, EPOLEAD D-210P, EPOLEAD PB3600, EPOLEAD PB4700, 10 etc. described in a catalog of Daicel Chemical Industries, Ltd.

[0038] Suitable monofunctional epoxy compounds include EX-111, EX-121, EX-141, EX-145, EX-146, EX-171, EX-192, EX-111 and EX-147, which are DENAKOL-series products 15 described in a catalog of Nagase Chemtex Co., Ltd.; and M-1230, EHDG-L and 100MF which are EPOLITE-series products described in a catalog of Kyoeisha chemical Co., Ltd. By using these substances as a reactive diluent, a highly viscous or solid epoxy resin can be used, for 20 example, BPF-type epoxy resins, BPA-type epoxy resins, BPF-type epoxy resins, novolak-type epoxy resins, brominated-type epoxy resins and flexible-type resins, which are described in a catalog of Tohto Kasei Co., Ltd.; EPIKOTE basic solid-type and EPIKOTE bis-F solid- 25 type described in a catalog of Yuka Shell Epoxy Kabushiki Kaisha; and EHPE alicyclic-type solid epoxy resins described in a catalog of Daicel Chemical Industries, Ltd.

[0039] As an oxetane compound, there may be used 30 compounds described in J. V. Crivello and H. Sasaki, J. M. S. Pure Appl. Chem., A30 (2&3), 189 (1993) or J. H. Sasaki and V. Crivello, J. M. S. Pure Appl. Chem., A30 (2&3), 915 (1993). Suitable examples include OXT-101 OXT- 121, OXT-211, OXT-221, OXT-212, OXT-611, etc. of Toa Gosei, Inc. These oxetane compounds may be used as a 35 mixture with the above-mentioned epoxy compound.

[0040] Suitable insolubilizing agents for cationic polymerization include, in addition to the above epoxy group and oxetane group compounds, monomers having a vinyl ether group, a propenyl ether group or a cyclic 5 ortho-ester group. Suitable vinyl ethers include butane diol divinyl ether, hexane diol divinyl ether, cyclohexane diol divinyl ether, diethylene glycol mono-vinyl ether, diethylene glycol divinyl ether, hydroxybutyl vinyl ether, hydroxyethyl vinyl ether, 10 octadecyl vinyl ether, butanediol monovinyl ether.

[0041] In the composition according to the present invention, a compound having at least one, more preferably at least two, formyl groups or acetal groups can be used as an acid reactive insolubilizing agent, 15 when using polyvinyl alcohol as the water-soluble resin. In this case, acetalization takes place on the poly(vinyl alcohol) chain with the acid generated serving as a catalyst, resulting in a water-insoluble product. Examples of suitable compounds having a formyl group 20 include salicylaldehyde, m-hydroxybenzaldehyde, p-hydroxybenzaldehyde, terephthalaldehyde, terephthalaldehyde bisethyl acetal, terephthalaldehyde trimethylene bisethylene acetal, glutaraldehyde bisdiethyl acetal and 25 glutaraldehyde bisethylene acetal.

[0042] A compound having at least one light-sensitive ethylenically unsaturated bond may be dissolved or dispersed in the photosensitive composition of the present invention. By addition of such a compound, not 30 only is an acid generated by the decomposition of photo-acid former but also free radicals are generated to initiate radical polymerization. The light-sensitive ethylenically unsaturated compound is a compound having at least one radical polymerizable unsaturated bond such 35 as an acryloyl group, a methacryloyl group or an allyl

group. The ethylenically unsaturated compound may be a prepolymer or an oligomer having a molecular weight of 10,000 or less.

[0043] Suitable unsaturated compounds include

5 pentaerythritol (meth)acrylate, pentaerythritol tetra (meth)acrylate, trimethylolpropane tri(meth)acrylate, triallyl isocyanurate, lauryl (meth)acrylate, methoxyethylene glycol (meth)acrylate, 2-ethylhexyl (meth)acrylate, benzyl (meth)acrylate, hexyl diglycol
10 (meth)acrylate, ethylene glycol di(meth)acrylate, diethylene glycol di(meth)acrylate, trimethylene ethylene glycol di(meth)acrylate, tetramethylene glycol di(meth)acrylate, pentamethylene glycol di(meth)acrylate, hexamethylene glycol di(meth)acrylate, ethylene glycol
15 digcidyl ether (meth)acrylate, phenyl glycidyl ether (meth)acrylate, trimethylolpropane polyglycidyl ether (meth)acrylate, terephthalic acid diglycidyl ether (meth)acrylate, a reaction product of tolylene diisocyanate and 2-hydroxypropyl (meth)acrylate, a
20 reaction product of phenyl isocyanurate and 2-hydroxyethyl (meth)acrylate and an unsaturated polyester with a molecular weight of 10000 or less and having an ethylenically unsaturated bond such as a maleic acid ester of glycol.

25 [0044] These light-sensitive unsaturated compounds may be used singly or in combination of two or more and are used in an amount of 0.5 to 5 parts, preferably 0.1 to 3 parts, per 1 part of the water-soluble resin.

[0045] These radical polymerizable compounds generate
30 not only acids but also free radicals when irradiated with light in the presence of a photo-acid former, alone or in combination with a sensitizer. Therefore, polymerization takes place to cause solubilization. Additionally, a known radical photoinitiator may be
35 cojointly used to facilitate the photo-radical reaction.

[0046] Next, a method for dispersing the above-described constituents in an aqueous solution of a water-soluble resin so as to obtain the composition of the present invention will be described.

5 [0047] The acid former, and optionally a sensitizer used, if necessary, by mixing therewith, are sparingly soluble or insoluble in water and are dispersed in an aqueous solution of a water-soluble resin after having been finely ground and further pulverized into a fine
10 powder. Alternately, these substances are pulverized in an aqueous solution of a water-soluble resin into a fine powder to obtain a suspension in which they are finely dispersed in a solid state. Since the composition of the present invention is used as a water suspension, it is
15 preferred that the acid former and/or sensitizer be finely dispersed in water. Therefore, as a dispersant, the water-soluble resin is suitably used, though a surfactant, etc., may also be used.

[0048] Thus, the present invention is characterized in
20 that a solid state photo-acid former is dispersed in water in the form of fine powder. To this end, known pulverization methods, dispersion methods and apparatuses therefor used for the manufacture of coating materials, pigments, inks, paints, various coatings, electronic
25 materials, magnetic materials, pharmaceuticals, agricultural chemicals, cosmetics, food, etc. may be utilized. Such methods and apparatus are disclosed in, for example, Taiichi TSURITANI and Masumi OISHI, "Industrial Dispersing Technique", Nikkan Kogyo Shimbun Ltd. (1985); Noboru MORIYAMA, "Chemistry of Dispersion and Aggregation", Sangyo Tosho Publishing (1995), p. 150-154; "Fine Particle Control" edited by Society of Chemical Engineers, Japan, Maki-Shoten Publishing (1996), p. 1-14; "Coating", edited by Processing Technique Study Group, Processing Technique Study Group (2002), p. 84-139.
30
35

Namely, devices such as a colloid mill, a ball mill, a sand mill, a bead mill, three roll mill and, additionally, a kneader, an extruder and a high speed disperser may be used singly or in combination. In dry type fine

5 pulverizing of the acid former and/or sensitizer, the pulverized fine powder is dispersed in an aqueous solution of a water soluble resin. In this case, the water soluble resin itself serves as a dispersant. If desired, a low molecular weight or high molecular weight

10 surfactant may be also added as a dispersant. In the case of wet pulverizing, since the pulverization and fine-dispersion are carried out in an aqueous solution of a water-soluble resin, a photosensitive composition can easily be prepared from the suspension itself. In this

15 case, too, a surfactant can be added in order to efficiently perform the dispersion.

20 **[0049]** The following methods may be employed for the

dry-type or wet-type pulverization of the photo-acid former in the presence of the spectral sensitizer:

25 **[0050]** In a first method, solids of the photo-acid former and sensitizer are pulverized together into fine powder in an aqueous solution of a water-soluble resin and dispersed therein. Namely, the photo-acid former and sensitizer in the form of a mixture are subjected to dry or wet fine pulverization.

30 **[0051]** In a second method, a mixture of the acid former and sensitizer are dissolved in an organic solvent. Thereafter, while removing the solvent from the solution or after the solvent has been removed therefrom, the mixture is finely dispersed in an aqueous solution of a water-soluble resin.

35 **[0052]** In a third method, the acid former agent and the sensitizer in the solid state are separately and finely dispersed in aqueous solutions of a water-soluble resin. Then, the resulting dispersions are mixed together.

[0053] In a further method for finely dispersing the acid former and/or sensitizer, a solution of them dissolved in an organic solvent is added dropwise to an aqueous solution of a water-soluble resin in accordance 5 with the method disclosed in Japanese Unexamined Patent Publication No. H06-79168 or No. 2001-262137.

[0054] The present inventors expected that, when a solid photo-acid is finely dispersed and the dispersion is irradiated an acid would be generated. However, they 10 unexpectedly found that the photo-sensitized acid-generation reaction occurs even when both the photo-acid former and the sensitizer are in the form of solids. That is, it had been accepted that in order for an electron transfer reaction or an energy transfer, which is a 15 sensitization reaction, to take place, it is necessary that the intermolecular distance between a molecule which gives electron or excitation energy (the molecule referred to as a "donor molecule") and a molecule which receives the electron or excitation energy (the molecule referred to as an "acceptor molecule") should be no more 20 than 10 angstroms. For this reason, it has been the general practice that the donor molecule and the acceptor molecule are combined into the same molecule, or are dissolved to a molecular concentration higher than a 25 predetermined level. It was therefore surprising that the radiation sensitized reaction occurs at a high rate, even though the photo-acid former and the sensitizer are dispersed as solids in the composition of the present invention, i.e., even though they are sparingly soluble 30 or insoluble in water. It is inferred that the acid former and the sensitizer might form an eutectic during the course of mixing and dispersing, or might form a solid solution with the acid-reactive insolubilizing agent and water-soluble resin during the course of a film 35 forming process.

[0055] Although the particle size of the acid former and/or sensitizer to be dispersed varies with the method and purpose of dispersing, the average particle diameter thereof is 1.5 μm or less, preferably 0.8 μm or less. The 5 particle size of the dispersed acid former and/or sensitizer is distributed. Therefore, photosensitivity is expressed even when the average particle diameter is, for example, 1.0 μm because of the presence of finer particles. If desired, after fully pulverizing and finely 10 dispersing the acid former and/or sensitizer in an aqueous solution of the water-soluble resin, large particles of the acid former and/or sensitizer may be removed by centrifugal separation or by filtration with a glass filter or a membrane filter, etc. It is known that 15 a transparent coloring agent is obtainable by removing the pigment particles having greater than a certain particle size, as described in Japanese Unexamined Patent Publication No. S60-129707. In the case of the present invention also, a photosensitive composition in which the 20 light scattering effect is remarkably reduced can be obtained by removing large particles of the photo-acid former and sensitizer.

[0056] It is desirable to add an antifoaming agent during or after the dispersing of the acid former and/or 25 sensitizer in an aqueous solution of the water-soluble resin. As the antifoaming agent suitable for the photosensitive composition of the present invention, there may be used antifoaming agents of a silicone-type and, additionally, antifoaming agents of an alcohol-type, 30 an ether-type, a metallic soap-type, an ester-type and a higher fatty acid-type, as described in "Application of Antifoaming Agent", Tsunetaka SASAKI (editor), CMC (1991).
[0057] To the thus obtained composition may be further added a water-soluble binder resin to adjust a property, 35 such as viscosity, of the photosensitive composition and

to improve the properties of the photosensitive film, such as mechanical strength, sensitivity and water resistance. As the binder resin, the water-soluble resin used as a dispersant can be used. It is desirable that 5 the resin have a high degree of polymerization.

[0058] In the formulation of the photosensitive composition of the present invention the amount of the acid-reactive insolubilizing agent is 5 to 1,000 parts, preferably 10 to 500 parts, per 100 parts of the water-soluble resin serving as a dispersant and a binder resin; 10 the amount of the acid former is 1 to 100 parts, preferably 5 to 50 parts, per 100 parts of the acid-reactive insolubilizing agent; the amount of the sensitizer is 5 to 100 parts, preferably 10 to 50 parts, 15 per 100 parts of the acid former; and the total amount of these ingredients is 5 to 400 parts, preferably 10 to 200 parts, per 100 parts of water. When the amount of the acid former and the acid-reactive insolubilizing agent is less than the above ranges, sufficient photo- 20 insolubilization does not occur, while the photo-insolubilization rate will not change even when the amounts thereof increase beyond the above ranges. When the amount of the sensitizer is less than the above range, sufficient sensitization is not obtainable. Even when the 25 amount of sensitizer added is above the foregoing range, the sensitization rate does not increase, but the light transmittance is undesirably reduced.

[0059] A finely dispersed extender such as aluminum oxide, silicon oxide, titanium oxide or zinc white may be 30 added to the photosensitive composition of the present invention. An organic pigment which does not have a sensitization effect on the acid former, such as a copper, nickel or iron complex of phthalocyanine, may also be added.

35 [0060] An aqueous resin emulsion the containing a

dispersoid of hydrophobic polymer particles can be added to the photosensitive composition of the present invention. The hydrophobic polymer of such an aqueous resin emulsion, may be poly(vinyl acetate), a polyvinyl acetate/ethylene polymer, a polyvinyl acetate/acrylic ester polymer, a styrene/butadiene copolymer, a methyl methacrylate/butadiene copolymer, an acrylonitrile/butadiene copolymer, a chloroprene copolymer, an isoprene copolymer, a poly(meth)acrylic resin, polyurethane, a polyester resin, poly(vinyl chloride), poly(vinylidene chloride), polystyrene, a silicone resin, polyethylene, a fluororesin, etc. These resin emulsions are used in an amount of 0.05 to 5 parts, preferably 0.1 to 3 parts, per 1 part of the water-soluble resin.

[0061] The photosensitive composition of the present invention is suitable for forming a coating (resin film) on any substrate such as: wood; textiles; paper; ceramics; glass; a synthetic resin, e.g. polyester, polyolefin, cellulose acetate, polyimide and epoxy resin; glass fiber reinforced resin; a metal, e.g. aluminum, copper, nickel, iron, zinc, magnesium and cobalt; a semiconductor material, e.g. silicon and gallium-arsenide-germanium; and an insulating material, e.g. silicon nitride and silicon oxide. It is desirable that the substrate be imparted with hydrophilicity beforehand, especially in the case of synthetic resin, for the purpose of improving the film forming efficiency. A pattern or a protective layer may be formed by irradiating the coating, made of the photosensitive composition of the present invention and formed on these substrates, with light.

[0062] The composition may be applied on a surface of the substrate by any known method capable of forming an uniform coating, such as by roller application, brushing,

spraying, reverse roll coating, dip coating, doctor knife coating or curtain coating. The average thickness of the film may range from 0.1 μm to 1,000 μm , though the thickness is dependent on the intended application, on 5 the type of substrate and on the particle size of the acid former or sensitizer.

[0063] The photosensitive composition applied on the substrate is exposed to light after evaporation of the water. The sensitization wavelength region is determined 10 by the type of the acid former and the sensitizer. Since a wide range of sensitizers can be used, the utilizable light wavelength ranges from far ultraviolet to infrared. Suitable light sources include low pressure mercury lamps, 15 high pressure mercury lamps, super-high pressure mercury lamps, xenon lamps, mercury-xenon lamps, halogen lamps, fluorescent lamps and various laser light sources which oscillate ultraviolet, visible or infrared radiation. The exposure may be through a photo mask. Alternatively, the photosensitive film may be directly patterned using a 20 laser beam. Exposure can also utilize electron beams or X-rays.

[0064] The portion(s) of the photosensitive film which has been exposed to light becomes insoluble in water. To facilitate the insolubilization, the light exposure may 25 be followed by a heat treatment. The temperature used in the heat treatment may vary depending upon the type of substrate but is generally in the range from room temperature to 250°C, preferably in the range from room temperature to 150°C. The heat treatment time depends 30 upon the type of the photosensitive composition and heating temperature, but is within the range of 30 seconds to 60 minutes.

[0065] The film which has been exposed to light and, if necessary, heat treatment, is developed with neutral 35 water. The development may be by immersing the

photosensitive film in water for dissolution and removal of the unexposed area or by contacting with a water spray from a spray gun for the removal of the unexposed area.

- [0066] A screen printing plate may be prepared by a conventional method which includes applying the photosensitive composition of the present invention over a screen, followed by drying, light exposure and development. Alternatively, a screen printing plate may be prepared by a conventional method which includes
- 5 applying the photosensitive composition on a plastic film, drying the coating to obtain a photosensitive film, applying the film on a screen plate using water, etc., drying the assembly, removing the plastic film, followed by light exposure and development.
- 10 [0067] Further, the radiation sensitive composition of the present invention may be used as an aqueous coating material. Thus, the composition is applied on a surface of a substrate, the coating being irradiated with ultraviolet, visible, or near infrared radiation or an
- 15 electron beam to harden the surface.
- 20

[0068] The radiation sensitive composition of the present invention offers the following advantages:

- [0069] (1) Since only water is used as a solvent for preparation of the radiation sensitive composition and for its development, the composition ensures the safety of work environment, fire prevention, prevention of pollution, etc.
- 25
- [0070] (2) The acid former can generate an acid, not only by the action of light, but also by the action of energy forms such as electron beams or X-rays.
- 30
- [0071] (3) Since various sensitizers can be used together, the composition obtained may be sensitive to radiation of a wide spectrum of wavelengths ranging from the far ultraviolet to the near infrared.
- 35

[0072] (4) The composition can be applied to a film or a screen substrate to form a radiation-sensitive film which serves as a photosensitive film capable of long term storage.

5 [0073] (5) A pattern of high resolution can be obtained by utilizing a small particle size of the water-insoluble or sparingly water-soluble acid former and of the sensitizer.

10 [0074] (6) The composition can provide a surface coating hardenable by light exposure or electron beam irradiation.

15 [0075] (7) The radiation-sensitive composition and a film obtainable therefrom can be advantageously utilized in the field of printing such as screen printing platemaking and also advantageously used as a coating composition, an adhesive composition, etc.

Examples:

20 [0076] The present invention will next be illustrated by working examples.

Examples 1 to 12

[0077] Preparation of Dispersions of Photo-Acid Former and Sensitizer:

25 [0078] A dispersion of a photo-acid former was prepared using a planetary-type fine pulverizer (Model P-7 manufactured by Fritsch Inc., Germany) and 45 mL pulverizing vessel made of stainless steel or zirconia in the following manner.

30 [0079] Poly(vinyl alcohol) (PVA, manufactured by Nihon Gosei Kagaku Co., Ltd.), as a dispersant, was dissolved in water to obtain a 15 % by weight aqueous solution. The aqueous solution (15 mL) and a photo-acid former and/or sensitizer were charged in the pulverizing vessel, to 35 which about 15 mL of stainless steel or zirconia

pulverizing beads, having a diameter of 5/32 inches and made of the same material as that of the pulverizing vessel, and an antifoaming agent (AQUAREN 1488 manufactured by Kyoeisha) were added. The vessel was 5 closed and rotated at a speed of 500 rpm for 5 minutes in one direction. Such a pulverization treatment was performed 4 times in total while alternately changing the rotational direction. Thereafter, the pulverizing beads were removed by filtration to obtain a photosensitive 10 dispersion. The thus obtained photosensitive dispersions were as shown in Table 1. The average particle diameter of the fine particles in the dispersions was 0.51 to 0.72 μm .

Table 1
Preparation of Dispersions of Photo-Acid Former and Sensitizer

Example	Dispersant: PVA solution	Photo-acid former and Amount added	Sensitizer and Amount added
1	10 parts by weight	Tribromomethylphenylsulfone: 4 parts by weight	
2	10 parts by weight	Bis(tert-phenyl)iodonium hexafluorophosphate: 4 parts by weight	
3	10 parts by weight	3-Methoxyphenylamine-4-diazonium hexafluorophosphate: 4 parts by weight	
4	10 parts by weight	2-(p-methoxyphenyl)4,6-bistrichloromethyltriazine: 4 parts by weight	
5	10 parts by weight	2-(2-(p-methoxyphenyl)ethenyl}4,6- bistrichloromethyltriazine: 4 parts by weight	
6	10 parts by weight	Dimethylphenacyl phosphonium tetra(pentafluorophenyl)borate: 4 parts by weight	
7	10 parts by weight		2-chlorothioxantone: 1 part
8	10 parts by weight	Tribromomethylphenyl sulfone: 4 parts by weight	9,10-diethoxyanthracene: 1 part by weight
9	10 parts by weight	Tribromomethylphenyl sulfone: 4 parts by weight	Bis(p-diethylamino)benzophenone: 1 part by weight
10	10 parts by weight	Tribromomethylphenyl sulfone: 4 parts by weight	3,3-Carbonylbis(7-diethylaminocoumarin): 1 part by weight
11	10 parts by weight	Tribromomethylphenyl sulfone: 4 parts by weight	2-Chlorothioxanthone: 1 part by weight
12	10 parts by weight	Bis(tert-phenyl)iodonium hexafluorophosphate: 4 parts by weight	3,3-Carbonylbis(7-diethylaminocoumarin): 1 part by weight

Examples 13 to 56

[0080] Preparation of Photosensitive Compositions:

[0081] While stirring the dispersion of the photo-acid former or sensitizer obtained in each of Examples 1 to 12,
5 an acid-reactive insolubilizing agent and an aqueous solution of a binder resin were added thereto. The acid-reactive insolubilizing agent used was N-methylolacrylamide (manufactured by Soken Chemical Co., Ltd.), methylolemelamine (M-3, manufactured by Sumitomo
10 Chemical Co., Ltd.), resol resin (RESITOP PL-4668, manufactured by Gun-ei Chemical Industry Co., Ltd.), methylolated urea (EX-211 or EX-321, manufactured by Nagase Chemtex Inc.) or an oxetane compound (OXT-121, manufactured by Toa Gosei Co., Ltd.). As an acrylic monomer, ethylene glycol diacrylate (PET-30, manufactured by Nippon Kayaku Co., Ltd.) was used. As the binder resin,
15 a 15 % by weight aqueous solution of K-217 (manufactured by Kuraray Co., Ltd) or a 10 % by weight aqueous solution of poly(vinyl alcohol) (PVA-SbQ) containing 1.4 mole %
20 stilbazolium substituent was used. As a resin emulsion, HA-100 manufactured by Clariant Polymer Co., Ltd. was used. To each of these photosensitive compositions, FL-GB blue (manufactured by Dainichiseika Kogyo Co., Ltd.) was added. The thus obtained photosensitive compositions were
25 as shown in Tables 2 to 5.

Table 2 Preparation of Photosensitive Compositions

Example	Photo-acid former dispersion	Acid-reactive insolubilizing agent	Binder resin
13	Sample of Example 1: 1 part by weight Sample of Example 7: 1 part by weight	N-methylolacrylamide: 1.5 parts by weight	K-217Aqueous solution: 100 parts by weight
14	Sample of Example 1: 1 part by weight Sample of Example 7: 1 part by weight	Methylol melamine: 1.5 parts by weight	K-217Aqueous solution: 100 parts by weight
15	Sample of Example 1: 1 part by weight Sample of Example 7: 1 part by weight	Methylolated urea: 1.5 parts by weight	K-217Aqueous solution: 100 parts by weight
16	Sample of Example 1: 1 part by weight Sample of Example 7: 1 part by weight	Resol resin: 1.5 parts by weight	K-217Aqueous solution: 100 parts by weight
17	Sample of Example 1: 1 part by weight Sample of Example 7: 1 part by weight	N-methylol acrylamide: 1.5 parts by weight	Aqueous solution of PVA-SbQ: 10 parts by weight
18	Sample of Example 2: 1 part by weight Sample of Example 7: 1 part by weight	N-methylol acrylamide: 1.5 parts by weight	K-217Aqueous solution: 100 parts by weight
19	Sample of Example 2: 1 part by weight Sample of Example 7: 1 part by weight	Methylolated urea: 1.5 parts by weight	K-217Aqueous solution: 100 parts by weight
20	Sample of Example 2: 1 part by weight Sample of Example 7: 1 part by weight	Resol resin: 1.5 parts by weight	K-217Aqueous solution: 100 parts by weight

[0082] Table 3 Preparation of Photosensitive Compositions

Example	Photo-acid former dispersion	Acid-reactive insolubilizing agent	Binder resin
21	Sample of Example 2: 1 part by weight	Epoxy compound: 40 parts by weight	K-217Aqueous solution: 100 parts by weight
	Sample of Example 7: 1 part by weight	Oxetane compound: 10 parts by weight	
22	Sample of Example 3: 1 part by weight	N-methylolacrylamide: 1.5 parts by weight	K-217Aqueous solution: 100 parts by weight
23	Sample of Example 3: 1 part by weight	Methylol melamine: 1.5 parts by weight	K-217Aqueous solution: 100 parts by weight
24	Sample of Example 3: 1 part by weight	Methylolated urea: 1.5 parts by weight	K-217Aqueous solution: 100 parts by weight
25	Sample of Example 3: 1 part by weight	Resol resin: 1.5 parts by weight	K-217Aqueous solution: 100 parts by weight
26	Sample of Example 3: 1 part by weight	Epoxy compound: 40 parts by weight	K-217Aqueous solution: 100 parts by weight
27	Sample of Example 3: 1 part by weight	N-methylol acrylamide: 1.5 parts by weight Terephthalaldehyde bisdiethyl acetal: 1.5 parts by weight	K-217Aqueous solution: 100 parts by weight
28	Sample of Example 4: 1 part by weight	N-methylol acrylamide: 1.5 parts by weight	K-217Aqueous solution: 100 parts by weight
29	Sample of Example 4: 1 part by weight	Methylol melamine: 1.5 parts by weight	K-217Aqueous solution: 100 parts by weight
30	Sample of Example 4: 1 part by weight	Methylolated urea: 1.5 parts by weight	K-217Aqueous solution: 100 parts by weight
31	Sample of Example 4: 1 part by weight	Resol resin: 1.5 parts by weight	K-217Aqueous solution: 100 parts by weight
32	Sample of Example 5: 1 part by weight	N-methylol acrylamide: 1.5 parts by weight	K-217Aqueous solution: 100 parts by weight
33	Sample of Example 5: 1 part by weight	Methylol melamine: 1.5 parts by weight	K-217Aqueous solution: 100 parts by weight
34	Sample of Example 5: 1 part by weight	Methylol melamine: 1.5 parts by weight Pentaerythritol acrylate: 1.5 parts by weight	K-217Aqueous solution: 100 parts by weight
35	Sample of Example 5: 1 part by weight	Resol resin: 1.5 parts by weight	K-217Aqueous solution: 100 parts by weight

[0083]

Table 4 Preparation of Photosensitive Compositions

Example	Photo-acid former dispersion	Acid-reactive insolubilizing agent	Binder resin
36	Sample of Example 6: 1 part by weight	N-methylol acrylamide: 1.5 parts by weight Diethylene glycol diacrylate: 1.5 parts by weight	K-217Aqueous solution:100 parts by weight
37	Sample of Example 6: 1 part by weight	Resol resin: 1.5 parts by weight	K-217Aqueous solution:100 parts by weight
38	Sample of Example 6: 1 part by weight	Epoxy compound: 40 parts by weight	K-217Aqueous solution:100 parts by weight
39	Sample of Example 8: 1 part by weight	N-methylol acrylamide: 1.5 parts by weight	K-217Aqueous solution:100 parts by weight
40	Sample of Example 8: 1 part by weight	Methylolated urea: 1.5 parts by weight	K-217Aqueous solution:100 parts by weight
41	Sample of Example 9: 1 part by weight	Methylolated urea: 1.5 parts by weight	K-217Aqueous solution:100 parts by weight
42	Sample of Example 9: 1 part by weight	Resol resin: 1.5 parts by weight	K-217Aqueous solution:100 parts by weight
43	Sample of Example 10: 1 part by weight	N-methylol acrylamide: 1.5 parts by weight	K-217Aqueous solution:100 parts by weight
44	Sample of Example 10: 1 part by weight	Methylolated urea: 1.5 parts by weight	K-217Aqueous solution:100 parts by weight
45	Sample of Example 11: 1 part by weight	N-methylol acrylamide: 1.5 parts by weight	K-217Aqueous solution:100 parts by weight
46	Sample of Example 11: 1 part by weight	Resol resin: 1.5 parts by weight	K-217Aqueous solution:100 parts by weight
47	Sample of Example 12: 1 part by weight	N-methylol acrylamide: 1.5 parts by weight	K-217Aqueous solution:100 parts by weight
48	Sample of Example 12: 1 part by weight	Methylol melamine: 1.5 parts by weight	K-217Aqueous solution:100 parts by weight
49	Sample of Example 12: 1 part by weight	Resol resin: 1.5 parts by weight	K-217Aqueous solution:100 parts by weight
50	Sample of Example 12: 1 part by weight	Epoxy compound: 40 parts by weight	K-217Aqueous solution:100 parts by weight
51	Sample of Example 12: 1 part by weight	Epoxy compound: 20 parts by weight Diethylene glycol diacrylate: 20 parts by weight	K-217Aqueous solution:100 parts by weight

[0084] Table 5

Example	Photo-acid Former dispersion	Acid-reactive insolubilizing agent	Resin emulsion	Binder resin
52	Sample of Example 8: 1 part by weight	N-methylol acrylamide: 1.5 parts by weight	HA-10: 15 parts By weight	K-217Aqueous solution: 100 parts by weight
53	Sample of Example 8: 1 part by weight	Methylolated urea: 1.5 parts by weight	HA-10: 15 parts By weight	K-217Aqueous solution: 100 parts by weight
54	Sample of Example 8: 1 part by weight	Resol resin: 1.5 parts by weight	HA-10: 15 parts By weight	K-217Aqueous solution: 100 parts by weight
55	Sample of Example 9: 1 part by weight	N-methylol acrylamide: 1.5 parts by weight	HA-10: 15 parts By weight	K-217Aqueous solution: 100 parts by weight
56	Sample of Example 10: 1 part by weight	Methylol melamine: 1.5 parts by weight	HA-10: 15 parts By weight	K-217Aqueous solution: 100 parts by weight

Comparative Examples 1 to 4

[0100]

- 5 Photosensitive compositions prepared without using the acid-reactive insolubilizing agent or using only a radical polymerizable monomer are shown in Table 6 as comparative examples.

10 Table 6 Preparation of Photosensitive Films

Comparative Example	Photo-acid former dispersion	Additive	Binder resin
1	Sample of Example 3: 1 part by weight	None	K-217Aqueous solution: 100 parts by weight
2	Sample of Example 3: 1 part by weight	Diethylene glycol diacrylate: 15 parts by weight	K-217Aqueous solution: 100 parts by weight
3	Sample of Example 8: 1 part by weight	Diethylene glycol diacrylate: 20 parts by weight	K-217Aqueous solution: 100 parts by weight
4	Sample of Example 10: 1 part by weight	Diethylene glycol diacrylate: 20 parts by weight	K-217Aqueous solution: 100 parts by weight

Examples 57 to 104

[0101] Preparation of Photosensitive Films and Photosensitization Characteristics:

- [0102] The photosensitive compositions obtained in Examples 13 to 56 were each applied onto a polyester film. The coatings were dried at 40°C for 15 minutes to obtain photosensitive films having thicknesses of 25 to 30 µm. Each film was irradiated through a photomask placed in contact therewith using a 4 KW high pressure mercury lamp or a 3 KW halogen lamp spaced a distance of 1 m therefrom. After irradiation, water was sprayed thereon using a spray gun to effect development. Prior to the development with water, a heat treatment was carried out for given temperature and time, when needed. The results are summarized in Tables 7 and 8, in which the evaluation of image formation is rated as follows:
- [0103] yes: negative pattern is obtained
- [0104] no: pattern is not formed
- [0105] Good patterns were obtained when the acid-reactive insolubilizing agent was used. When no acid-reactive insolubilizing agent was added or when only a radical polymerizable monomer was added, negative patterns were not obtained.

Table 7 Photosensitization Characteristics of Films obtained from Photosensitive Compositions

Example	Photosensitive Composition Preparation Example	Light Source	Exposure Time (min.)	Heat treatment condition	Image formation
57	Example 13	Mercury lamp	3	80°C, 10 minutes	A
58	Example 14	Mercury lamp	3	80°C, 10 minutes	A
59	Example 15	Mercury lamp	3	40°C, 20 minutes	A
60	Example 16	Mercury lamp	3	40°C, 20 minutes	A
61	Example 17	Mercury lamp	2	40°C, 20 minutes	A
62	Example 18	Halogen lamp	3	40°C, 20 minutes	A
63	Example 19	Halogen lamp	3	40°C, 20 minutes	A
64	Example 20	Halogen lamp	3	40°C, 20 minutes	A
65	Example 21	Halogen lamp	3	Room temperature 120 minutes	A
66	Example 22	Mercury lamp	2.5	80°C, 10 minutes	A
67	Example 23	Mercury lamp	2.5	80°C, 10 minutes	A
68	Example 24	Mercury lamp	2.5	40°C, 20 minutes	A
69	Example 25	Mercury lamp	2.5	40°C, 20 minutes	A
70	Example 26	Mercury lamp	2.5	40°C, 20 minutes	A
71	Example 27	Mercury lamp	2.5	40°C, 20 minutes	A
72	Example 28	Mercury lamp	4	80°C, 5 minutes	A
73	Example 29	Mercury lamp	3	80°C, 5 minutes	A
74	Example 30	Mercury lamp	3	80°C, 5 minutes	A
75	Example 31	Mercury lamp	3	80°C, 5 minutes	A
76	Example 32	Mercury lamp	3	80°C, 5 minutes	A
77	Example 33	Mercury lamp	2.5	80°C, 5 minutes	A
78	Example 34	Mercury lamp	2.5	80°C, 5 minutes	A
79	Example 35	Mercury lamp	2.5	40°C, 20 minutes	A
80	Example 36	Mercury lamp	1	40°C, 20 minutes	A

[0106]

Table 8 Photosensitization Characteristics of Films obtained from Photosensitive Compositions

Example	Photosensitive Composition Preparation Example	Light Source	Exposure Time (min.)	Heat treatment condition	Image formation
81	Example 37	Mercury lamp	2.5	40°C, 20 minutes	A
82	Example 38	Mercury lamp	2	40°C, 20 minutes	A
83	Example 39	Halogen lamp	2	40°C, 20 minutes	A
84	Example 40	Halogen lamp	2	40°C, 20 minutes	A
85	Example 41	Halogen lamp	1.5	80°C, 20 minutes	A
86	Example 42	Halogen lamp	1.5	40°C, 20 minutes	A
87	Example 43	Halogen lamp	1.5	40°C, 20 minutes	A
88	Example 44	Halogen lamp	1	Room temperature 120 minutes	A
89	Example 45	Mercury lamp	3	40°C, 20 minutes	A
90	Example 46	Mercury lamp	3	40°C, 20 minutes	A
91	Example 47	Mercury lamp	1	40°C, 20 minutes	A
92	Example 48	Mercury lamp	1	80°C, 10 minutes	A
93	Example 49	Mercury lamp	1	80°C, 10 minutes	A
94	Example 50	Mercury lamp	1	40°C, 20 minutes	A
95	Example 51	Mercury lamp	1	40°C, 20 minutes	A
96	Example 52	Mercury lamp	2	40°C, 20 minutes	A
97	Example 53	Mercury lamp	2	80°C, 10 minutes	A
98	Example 54	Mercury lamp	2	80°C, 10 minutes	A
99	Example 55	Mercury lamp	1.5	40°C, 20 minutes	A
100	Example 56	Mercury lamp	1	40°C, 20 minutes	A
101	Comparative Example 1	Mercury lamp	10	40°C, 20 minutes	B
102	Comparative Example 2	Mercury lamp	5	40°C, 20 minutes	B
103	Comparative Example 3	Mercury lamp	10	40°C, 20 minutes	B
104	Comparative Example 4	Mercury lamp	5	80°C, 10 minutes	B

5 Examples 105 to 117

[0107] Preparation of Films for Screen Platemaking and Photosensitization Characteristics:

[0108] The photosensitive compositions obtained in the above examples were each applied onto a 250 mesh polyester screen and then dried. Such application and drying

operations were repeated to obtain uniform films having thicknesses of about 15 μm . Each film was irradiated through a photomask placed in contact therewith using a 4 KW high pressure mercury lamp or a 3 KW halogen lamp spaced a distance of 1 m therefrom. After irradiation, water was sprayed thereon using a spray gun to effect development. Prior to the development with water, a heat treatment was carried out for given temperature and time, when needed. The results are shown in Table 9. The patterns obtained exhibited good water resistance and show good resistance against organic solvents such as toluene, acetone, ethyl acetate and butyl cellosolve. When the compositions of Comparative Examples were used, however, patterns were not formed by water development after exposure.

Table 9 Sensitization Characteristics of Films for Screen Platemaking obtained from Photosensitive Composition

Example	Photosen-sitive Compo-sition Prepa-ration Example	Light Source	Expo-sure Time (min.)	Heat treatment condition	Image Form-ation	Water Resis-tance	Sol-vent resis-tance
105	Example 13	Mercury lamp	3	40°C, 20 minutes	A	A	A
106	Example 21	Mercury lamp	3	40°C, 20 minutes	A	A	A
107	Example 22	Mercury lamp	3	40°C, 20 minutes	A	A	A
108	Example 26	Mercury lamp	4	40°C, 30 minutes	A	A	A
109	Example 28	Mercury lamp	1	40°C, 20 minutes	A	A	A
110	Example 36	Mercury lamp	2	40°C, 20 minutes	A	A	A
111	Example 38	Mercury lamp	2	40°C, 20 minutes	A	A	A
112	Example 42	Mercury lamp	1.5	40°C, 20 minutes	A	A	A
113	Example 50	Mercury lamp	2	40°C, 30 minutes	A	A	A
114	Example 51	Mercury lamp	2	40°C, 30 minutes	A	A	A
115	Example 52	Mercury lamp	1.5	40°C, 20 minutes	A	A	A
116	Comp. Example 1	Mercury lamp	10	40°C, 20 minutes	B	B	B
117	Comp. Example 1	Mercury lamp	10	40°C, 20 minutes	B	B	B